An electron paramagnetic resonance study of $Pr_{0.6}Ca_{0.4}MnO_3$ across the charge ordering transition

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Abstract

We report the first electron paramagnetic resonance studies of single crystals and powders of $Pr_{0.6}Ca_{0.4}MnO_3$ in the 300-4.2 K range, covering the charge ordering transition at $\sim$ 240 K and antiferromagnetic transition (T_N) at $\sim$ 170 K. The asymmetry parameter for the Dysonian single crystal spectra shows anomalous increase at T_{co}. Below T_{co} the g-value increases continuously, suggesting a gradual strengthening of orbital ordering. The linewidth undergoes a sudden increase at T_{co} and continues to increase down to T_N. The intensity increases as the temperature is decreased till T_{co} due to the renormalization of magnetic susceptibility arising from the build up of ferromagnetic correlations. The value of the exchange constant, J, is estimated to be 154 K.

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Recent investigations of rare earth manganites and related systems exhibiting colossal magnetoresistance has led to the discovery of interesting phenomena related to charge, spin and orbital ordering in these materials[1]. Phase diagrams of these systems as a function of

doping and temperature are therefore very interesting showing regimes of varied magnetic and electrical properties. These manganites of general composition $A_{1-x}A'_x MnO_3$ where A is a trivalent rare earth ion (e.g La, Pr, Nd etc) and A' is a divalent ion (e.g Ca, Sr, Pb etc) show a rich phase diagram[2] depending on the tolerance factor and the amount of doping x which, in turn, controls the ratio of Mn^{3+} to Mn^{4+}. The end members of this series i.e x=0 and x=1 are A type and G type antiferromagnetic insulators (AFI), respectively. For 0.17 < x < 0.5 the system undergoes a metal to insulator (MI) transition as the temperature is increased. This MI transition also coincides with the magnetic transition from the ferro to the paramagnetic state. Electronic properties of these systems are understood qualitatively in terms of the Zener's double exchange interaction[3-5] (DEX). In DEX there is a strong Hund's coupling between the 3 t_{2g} electrons whose spins are parallel and constitute a core spin of 3/2 and the lone e_g spin. This e_g electron can hop from one Mn^{3+} site to adjacent Mn^{4+} site via the intermediate oxygen when the core spins are parallel which also implies that metallicity coincides with ferromagnetism. To explain the resistivity data, Millis et al[6] invoked the localization of charge carriers above T_c due to polaron formation. In the case of systems where the weighted average A site cation radius is small, the system also shows charge ordering (CO) i.e real space ordering of Mn^{3+} and Mn^{4+} ions, as a function of temperature. The CO state becomes stable when the repulsive Coulomb interaction between carriers is dominant over the kinetic energy. In these types of cases there is a strong competition between the double exchange interaction which favours ferromagetism and CO which favours antiferromagnetism. The smaller size of A site cation leads to a deviation in the Mn-O-Mn bond angle from 180° resulting in lowering of the transfer integral. This in turn implies a lower band width of the e_g electron and hence higher electronic correlations in the system. The stability of the CO state depends on the commensurability of the carrier concentration with the periodicity of the crystal lattice and is stable for x=0.5.

$Pr_{1-x}Ca_x MnO_3$ shows a rich phase diagram as a function of doping and temperature and is well studied using a variety of probes like resistivity[7], magnetization[8], neutron diffraction studies[9-12] and transmission electron microscopy[13]. For x=0.4, the sample is insulating at all

temperatures in zero field. The resistivity changes by more than six orders of magnitude from 300 K to 50 K. There is a perceptible change in slope at around $T_{CO} \sim 240$ K signifying the onset of charge ordering. In the temperature range $T > T_{co}$ (240 K) the system is a paramagnetic insulator. In dc magnetic susceptibility, a large peak is observed at T_{co} followed by a relatively small peak at T_N. The peak at T_{co} is attributed to ferromagnetic correlations[10]. The system further undergoes a transition at 170 K to a CE type AFI. The pseudo CE type structure for x < 0.5 is different than the CE structure present in systems with x = 0.5. In this so called "pseudo CE" structure the zig-zag FM chains in the ab plane are FM aligned along the c axis[10]. This is unlike the CE structure where the layers in the ab plane are aligned antiferromagnetically along c. Further lowering of temperature below 50 K leads to another transition which can be understood either as a canted antiferromagnetic state[11,12] or as a mixture of ferromagnetic domains or clusters in an antiferromagnetic background. In this paper we report our EPR study of single crystals as well as powders of $Pr_{0.6}Ca_{0.4}MnO_3$ as a function of temperature from 300 K to 4.2 K. Although several EPR studies on the manganites have been reported recently across the metal-insulator transition[14−21], to our knowledge, there has been no study across the CO transition. The dynamics of spins in the charge ordered state as studied by EPR is expected to throw some light on the controversial magnetic structure between the charge ordering transition and the Neel temperature.

The single crystal used for the experiment was prepared by the float zone technique and characterized using dc magnetic susceptibility which shows a large peak at 240 K (T_{co}) and a relatively small peak at 170 K (T_N). The measurements on single crystals were done with magnetic field parallel to (100) axis. Powder of the material was dispersed in paraffin wax for study. The EPR measurements were carried out at 9.2 GHz (X band) with a Bruker spectrometer (model 200 D) equipped with an Oxford Instruments continous flow cryostat (model ESR 900), with a temperature accuracy of ± 2 K.

Fig. 1 shows the EPR spectra at a few temperatures in the range 300 K to 180 K recorded in the heating run for a single crystal (fig. 1(a)) and a powder sample (fig. 1(b)).

The ESR signal could be observed only above 180 K. The observed signals are very broad. The spectra from the single crystal are Dysonian in shape and were fitted (solid lines in Fig. 1(a)) to a functional form similar to the one used by Ivanshin et al[21] for $La_{1-x}Sr_xMnO_3$. The field derivative of the power absorbed given by

$$\frac{dP}{dH} \propto \frac{d}{dH}\left(\frac{\Delta H + \alpha(H - H_{res})}{(H - H_{res})^2 + \Delta H^2} + \frac{\Delta H + \alpha(H + H_{res})}{(H + H_{res})^2 + \Delta H^2}\right) \tag{1}$$

incorporates responses to both the circular components of the exciting linearly polarised microwave field. The above equation also includes both absorption and dispersion. α, the asymmetry parameter is a measure of dispersion-to-absorption ratio. The spectra from powder samples are symmetrical and were well fitted with Lorentzians as shown in Fig. 1(b).

Careful EPR measurements in doped manganites by Causa et al[17] and Lofland et al[20] show that that both Mn^{3+} and Mn^{4+} contribute to the EPR signal. The bottleneck model used by Shengalaya et al[19] also shows that the EPR intensity is proportional to the total susceptibility of the Mn^{4+} and Mn^{3+} spins. We will first discuss our results on temperature dependence of EPR lineshape parameters of single crystals.

Fig. 2 shows the temperature dependence of the lineshape parameters of the signals obtained by fitting to equation (1). Fig. 2(a) shows the temperature dependence of the linewidth (Δ H). The linewidth decreases as the temperature is lowered from 300 K upto just above T_{co} and then nearly doubles across the charge ordering transition. This increase is somewhat similar to that observed[19] in $LaCaMnO_3$ across the paraamgnetic insulator to ferromagnetic metal transition, thereby implying a buildup of spin-correlations at T_{co}. The increase in linewidth above T_{co} can be interpreted in terms of spin-lattice relaxation or even as an opening up of the "bottleneck" as the temperature is raised[19,20]. Fig. 2(c) shows the variation of the integrated intensity as a function of temperature. We have tried to analyse the temperature dependence of intensity in terms of the bottleneck model[19,25]. In this picture, the EPR signal originates from both Mn^{4+} and Mn^{3+} ions and the intensity is proportional to the total susceptibility. Here the spin-spin relaxation rates between the

exchange coupled Mn^{3+} and Mn^{4+} ions are much larger than the spin-lattice relaxation rates. In this regime the ferromagnetic correlations will renormalize the spin susceptibility given by[19]

$$I \propto \chi_{total} = \chi_s + \chi_\sigma \tag{2}$$

where χ_s and χ_σ are the renormalised static susceptibilities and are given by

$$\chi_s = \chi_s^o \frac{1 + \lambda \chi_\sigma^o}{1 - \lambda^2 \chi_\sigma^o \chi_s^o}, \qquad \chi_\sigma = \chi_\sigma^o \frac{1 + \lambda \chi_s^o}{1 - \lambda^2 \chi_\sigma^o \chi_s^o} \tag{3}$$

where χ_s^o = bare spin susceptibility of Mn^{4+} and χ_σ^o = bare spin susceptibilty of Mn^{3+}. The parameter $\lambda = zJ/Ng_sg_\sigma\mu_B^2$, where J is the exchange coupling constant between Mn^{4+} and Mn^{3+} spins, g_s (g_σ) is the g factor of Mn^{4+} (Mn^{3+}) ions ,N is the number of spins per cm^3, z number of nearest neighbours and μ_B is the Bohr magneton. We can get some estimate of J by fitting Eqs. 2 and 3 to the data in Fig 2(c). Taking $g_s = g_\sigma = 2$, $z = 6$ and assuming that the bare susceptibility of Mn^{4+} ions is given by Curie law $\chi_s^o = C_s/T$ while that of Mn^{3+} follows a Curie-Weiss law $C_\sigma/(T-\Theta)$, where Θ, the negative Curie Weiss temperature is taken to be the same as that in undoped $LaMnO_3$ (Θ = -100 K). The solid line shows the fit to the intensity data above T_{co} yielding an estimate of $J \sim 154 \pm 1.24$ K. This value is of the same order of magnitude as the value obtained for J (~ 70 K) in doped manganites by EPR measurements[19], neutron scattering[26] and Brillioun scattering experiments[27]. At this stage we would also like to point out that though all spins contribute to the EPR intensity, the temperature dependence is qualitatively different from the dc susceptibility data (as shown in inset of Fig2(c)) . This could be due the fact that the resistivity of the sample is increases by two orders of magnitude in the temperature regime of 300-180 K which will enhance the penetration depth and hence the volume of sample seen by the microwave field is changing with temperature. Fig 2(b) shows the temperature variation of g value. Since internal field effects can influence the single crystal data, we will focus our attention on temperature variation of g only in the powder data.

'Asymmetry parameter', α of the signals, from single crystal data is shown in Fig. 3. The ratio remains practically constant from 300 K to T_{co} where it discontinously increases

from ~ 2.5 to ~ 4.5. Further cooling results in a decrease of α value towards unity as is to be expected from the decrease in conductivity at lower temperatures (resistivity[22] shown in inset of Fig. 3). The discontinous *increase* of α at T_{co} is interesting because normally one would have expected a decrease following the decrease in conductivity. However as shown by Dyson[23] and Feher and Kip[24] the value of α depends also on the ratio of the time T_D taken by the electrons to diffuse through the skin depth and the spin-spin relaxation time T_2. The sudden increase in α therefore indicates a sudden dip in the value T_D/T_2. This implies that the value of T_2 increases at T_{co} to offset the increase in T_D due to decrease in the conductivity. However, this is contrary to the observed increase in the linewidth at T_{co}. At present, we do not have a satisfactory explaination of this result.

Fig 4 shows the temperature dependence of the lineshape parameters for the powder sample extracted by fitting derivative of the Lorentzian function yielding temperature dependence of the linewidth (ΔH), resonance field (H_o) and area under the curve. Fig. 4(b) shows the temperature dependence of the g factor, estimated from the resonance field. In all the earlier EPR reports in manganites, the value of g was observed to be close to or less than that of free electron (= 2.0023). Earlier EPR studies on Mn^{3+} and Mn^{4+} dilutely doped in diamagnetic hosts have given[28] g ~ 1.98. However our experiments give a g value higher than that for the free electrons for all temperatures. A speck of DPPH (g = 2.0036) was used as a g-marker and the centre resonance field was obtained from the fit to the Lorentzian. This procedure gives confidence in our measurements of temperature dependence of g. Since the internal field effects are expected to average out in powdered samples, we believe that the increase in g for $T < T_{co}$ is intrinsic in nature. One possible reason can be the changes in the spin-orbit coupling. It is known that $g_{eff} = g[1 \pm \kappa/\Delta]$, where the spin orbit interaction energy is $\kappa \vec{L}.\vec{S}$ and Δ is the appropriate crystal field splitting[29]. A recent transmission electron microscopy study[13] of $Pr_{0.5}Ca_{0.5}MnO_3$ has shown that the incommensurate to commensurate charge ordering is coincident with paramagnetic to antiferromagnetic transition at 180 K. The physical picture is that for $T_N < T < T_{co}$, orbital ordering is partial inspite of complete charge ordering. This orbital ordering builds up

and is complete at T_N. Therefore for $T < T_{co}$ a gradual buildup of the orbital ordering can change the spin-orbit coupling and lead to an increase in the value of g as the temperature is lowered. This may also be the reason for the sign of g shift with respect to the free electron g which is opposite to that expected for Mn^{3+} and Mn^{4+} ions (less than half filled d-shells). It will be very interesting to theoretically calculate the value of g, incorporating orbital ordering. Fig. 4(a) shows the temperature variation of the full width at half maximum of the Lorentzian, ΔH. For $T > T_{co}$, the width decreases linearly as the temperature is lowered from 300 to 240 K similar to that observed in single crystal data. Below T_{co} till 180 K, the width increases significantly (almost by a factor of 2). It is remarkable that the width increases sharply from $\sim$ 1600 G at 240 K to $\sim$ 2200 G at 228 K. This sharp increase can be due to magnetic fluctuations which are also responsible for the peak in the dc magnetic susceptibility. The further increase in ΔH as temperature is lowered can arise due to build up of magnetic correlations preceeding the transition to the long range antiferromagnetic ordering at 170 K. Fig. 4(c) shows the temperature dependence of the intensity which is qualitatively similar to that of single crystal data.

In summary, we have reported for the first time EPR measurements on charge-ordered $Pr_{0.6}Ca_{0.4}MnO_3$. The lineshape parameters reveal a rich temperature dependence across T_{co} as well as at lower temperatures approaching T_N. The intensity variation above T_{co} is considered to be due to the renormalization of spin susceptibility due to ferromagnetic (FM) correlations. Such FM correlations in the paramagnetic insulating phase have been invoked to understand the origin of the peak in magnetic susceptibility near T_{co} and of dynamical spin fluctuations above T_c in doped manganites[30,31]. The formation of magnetic polarons to localize the carriers has been suggested by Varma et al[32]. The value of exchange coupling constant J is estimated to be about 154 K. The fluctuations in the magnetic correlations near the transition temperatures lead to a large increase in the linewidth. The temperature dependence of the g factor suggests a need to carry out theoretical calculations of g invoking orbital ordering.

FIGURES

FIG. 1. Derivative spectra of $Pr_{0.6}Ca_{0.4}MnO_3$ for (a) single crystal and (b) powder sample at a few select temperatures. The signal from DPPH has been subtracted from fig. 1(b). The solid lines shows the Dysonian and Lorentzian fits to the crystal and powder sample data respectively.

FIG. 2.   Variation of the lineshape parameters - linewidth, g and intensity as a function of temperature for the single crystal data obtained by fitting to eq. (1) . The solid line in Fig. 2(c) shows the fit for $T > T_{co}$ to Eq. 2 and 3 as discussed in the text. Inset shows the temperature variation of dc magnetic susceptibility.

FIG. 3.   Variation of asymmetry parameter α as a function of temperature for single crystal data. The inset shows the temperature dependence of resistivity (taken from Ref. 22).

FIG. 4. Lineshape parameters for powder sample - linewidth, g and intensity as a function of temperature obtained by fitting spectra to a Lorentzian profile.

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CRYSTAL **(a)**

POWDER **(b)**

290K

250K

240K

210K

185K

dP/dH (arb. units)

0 1750 3500 5250 0 1750 3500

Magnetic Field (Gauss)